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Inter-Layer Coupling Induced Bandgap Reduction in Ultrathin MoS_2

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We report on a study of highly crystalline islands of MoS_2 grown on HOPG substrate. Using STM/STS we find that the valence band edge shifts as a function of the layer number. Numerical calculations reveal the mechanism underlying the bandgap reduction and the role of the interfacial Sulfur atoms is clarified.

Two-dimensional transition metal dichalcogenides are layered materials typically composed of planar sheets with strong in-plane bonds and with layers weakly bound by van der Waals interactions. In this work we report a systematic study of the evolution of electronic properties of ultrathin MoS_2 films as a function of layer number [1]. We utilize scanning tunneling microscopy and spectroscopy (STM/STS) measurements in order to address nanoscale properties of MoS_2. Experimental data are modeled within a tight-binding framework to unfold the mechanism responsible for reduction in the band gap with film thickness.

Figures 1(a,b) show large-scale STM topographies of stacked MoS_2 sheets on HOPG. Atomic resolution STM images taken on the substrate and MoS_2 terraces allow to distinguish MoS_2 and HOPG substrate. In order to elucidate the thickness-dependent electronic properties of MoS_2, local STS measurements were performed on the first three layers in Figures 1(a,b). On *dI/dV* curves shown in Figure 1(c) the edge of the valence band maximum (VBM) on the first MoS_2 layer is located at 1.79 eV below the Fermi level (E_F), and the conduction band minimum (CBM) is located at 0.27 eV above the E_F. The spectra show a reduction of the band gap as the thickness increases which is mostly due to a shift of the valence band edge from -1.79 eV to -1.62 eV from the monolayer to the bilayer, while the transition from two to three layers presents a more subtle decrease. The conduction band edge remains fixed at +0.27±0.05 eV.

The computational studies were performed within the framework of a realistic, Slater-Koster type tight-binding model Hamiltonian in which the overlap amplitudes were obtained through fits to first-principles band structures of one- and several-layer thick MoS_2 films using WANNIER90 and VASP codes. Band structure computations show that band gap changes abruptly as we go from one to two layer MoS_2 film. In the one layer system, the band gap is direct at the K-point, but for two or more layers, the band gap becomes indirect as the valence bands move to higher energies at Γ-point. The fundamental mechanism responsible for the dependence of the spectral gap on layer thickness becomes obvious when we consider contributions of different orbitals to the electronic states in the vicinity of the E_F. In the one-layer film, the maximum of the valence band at the K point has a distinct Mo d_{xy} and d_{x2-y2} orbital character, while the states at the Γ-point have a strong Mo d_{z2}-character mixed with S-p_z orbitals. In the two-layer system, on the other hand, the orbitals of interfacial S atoms overlap with each other, making the states at Γ-rehybridize. The surface and interface S atoms contribute to

different bands: the top of the valence band at the Γ-point now originates from the interfacial S and the adjoining Mo atoms, while the surface S atoms contribute only weakly to the top of the valence band.

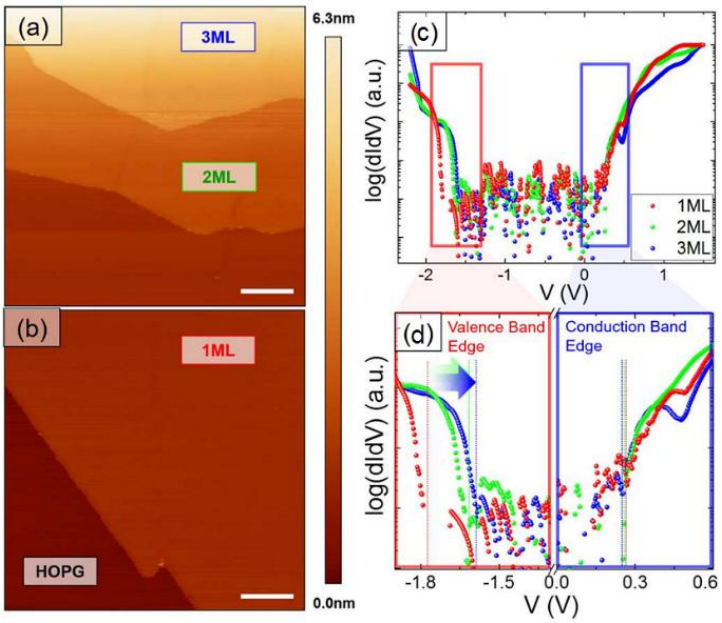

Figure 1. STM/STS characterization of MoS_2 films. (a) and (b) STM topography showing terraces of MoS_2, the underlying graphite can be seen in the bottom part of (b). The scale bar represents 50nm. (c) STS spectra reveal a reduction in the band gap with increasing layer number (set point: V=+1.5 V, I=200 pA). (d) Valence and conduction band edges in panel (c) are magnified to highlight their evolution with layer number.

In this high-resolution STM/STS study, we have investigated the intrinsic electronic properties of atomically thin MoS_2 layers. The electronic bandgap of the single layer MoS_2 is determined to be 2.06 eV by STS spectra taken at 4.2 K, and it is suppressed by approximately 0.17 eV in the bilayer. The band gap decrease is mostly due to a valence-band-edge shift. Parallel computational modeling of the electronic structure of the films and the associated STS spectra reveals that the interfacial S atoms are mainly responsible for the change in band structure and the observed shift of the valence band edge.

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